

Reaction transport modelling of a freshening aquifer (Tertiary Ledo-Paniselian Aquifer, Flanders-Belgium)

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Abstract

The semi-confined Ledo-Paniselian (Eocene) Aquifer in Flanders, Belgium is recharged in the areas with higher topography, where it is covered by the Bartonian Clay. Initial conditions in these sediments were marine. Hydrogeochemical modelling of the groundwater type distribution in the aquifer with a reaction transport model considers recharge of fresh CaHCO_3 water by downward flow through the overlying clay. In the aquifer, in an upstream direction, progressively more freshened water types are found. A typical NaHCO_3 type occurs upstream of the brackish-fresh water interface. The different stages of cation exchange produce a chromatographic sequence of groundwater types, which agrees well with observations. Cation exchange processes occurring mainly in the percolated clay, result in a Na^+ increase, and peaks of K^+ , NH_4^+ and Mg^{2+} in the aquifer, which are spatially separated as a result of groundwater flow. Calcite equilibrium, gypsum dissolution in the clay and sulphate reduction in the aquifer have also been included in the modelling.

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1. Introduction

The objective of this paper is to show the control of cation exchange reactions on the groundwater chemistry of the sandy Ledo-Paniselian Aquifer in Flanders (Belgium). Marine conditions (represented by a marine interstitial solution and marine cations, Na^+ , K^+ and Mg^{2+} , adsorbed onto clay minerals) prevailing in the sediments before the last regression

at the end of Tertiary times, are being gradually expelled by infiltrating fresh water. Cation exchange processes by fresh water intrusion in detrital marine sediments have been well documented by previous studies in other areas, such as aquifers in coastal plains in the United States (Foster, 1950; Back, 1966; Chapelle and Knobel, 1983; Appelo, 1994a), in polder areas in The Netherlands (Appelo and Willemssen, 1987; Beekman, 1991; Stuyfzand, 1993) and in Tertiary sediments in Flanders, Belgium (Walraevens, 1987, 1990).

The displacement of interstitial sea water by fresh water in marine sediments results in a typical NaHCO_3 type water upstream of the salt- or brackish-fresh water interface. Furthermore a

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chromatographic pattern can appear upstream of the salt- or brackish-fresh water interface when a sequence of Na^+ , K^+ , Mg^{2+} and finally Ca^{2+} type waters is developed. Column experiments in the laboratory (Appelo et al., 1990; Beekman and Appelo, 1990; Beekman, 1991) and short term field tests (Valocchi et al., 1981) have shown the existence of chromatographic patterns when sediments with high exchange capacity, equilibrated with salt or brackish water, are flushed with fresh water.

In aquifers the chromatographic pattern may be obscured by flow conditions in the aquifer (for example, mixing of waters of different origin) which change the relative concentrations of the cations Ca^{2+} , Mg^{2+} , Na^+ and K^+ . So the chromatographic patterns are difficult to detect in actual conditions. But confirmation of this theory has been described in detritic aquifers in the United States (Aquia Aquifer in Maryland, Appelo, 1994a), Dutch polders (Beekman, 1991; Stuyfzand, 1993) or marine sediments (alternating clayey and sandy layers) in Flanders, Belgium (Cardenal and Walraevens, 1994; Walraevens and Cardenal, 1994).

A reaction transport model, according to the terminology of Parkhurst and Plummer (1993), has been used to model geochemical reactions in the Ledo-Paniselian Aquifer in Flanders, Belgium, including advection and dispersion processes. During recharge of the aquifer, succeeding water types will develop and be displaced with time because of changes in the exchange complex and groundwater motion. This non-steady state with respect to the chemical groundwater compositions in the Ledo-Paniselian Aquifer renders it impossible to use mass balance calculations. But the reaction transport approach employed permits spatial and temporal analysis of the reactions involved in the aquifer.

2. Geology and hydrogeology of the Ledo-Paniselian Aquifer

The survey area comprises the northern part of the provinces of East- and West-Flanders in Belgium. The Eocene marine Ledo-Paniselian sediments are part of a sequence of alternating clayey and sandy subhorizontal Tertiary deposits that are gently dipping toward the NNE. The geology of the Tertiary surface below the Quaternary sediments is shown in Fig. 1. The Ledo-Paniselian Sands are overlain by the heavy Bartonian Clay, making the aquifer semi-confined. The depth to the top of the aquifer increases toward the NNE.

The Ledo-Paniselian Sands are underlain by the Paniselian Clay, followed by the Ieperian (or Ypresian) Sands and the Ieperian Clay. The latter is a stiff clay with a thickness of over 100 m, and can be considered as the base of the groundwater reservoir (Walraevens, 1987). The Bartonian Clay, confining the Ledo-Paniselian Aquifer, is composed of several units, of which units a1, a2, a3 are stiff clay, while Asb-a, s1 and s2 consist of sandy clay to clayey sand. Toward its southern boundary (Fig. 1), the Bartonian Clay is not developed over its full extent, so that e.g. at Ursel, it almost exclusively consists of the lowermost units Asb-a and a1 (Fig. 4).

In natural flow conditions, the semi-confined Ledo-Paniselian Aquifer is recharged in the topographically higher regions, in which recharge is occurring by infiltration through the Bartonian Clay. These recharge areas are shaded on the map in Fig. 1. The arrows indicate horizontal groundwater flow directions. They were derived from the piezometric map in Fig. 2a. This map has resulted from a 3D mathematical model of groundwater flow in the reservoir (Walraevens, 1988). It agrees well with piezometric observations, taken at a time before groundwater flow was substantially influenced by pumping (mostly around 1920). High hydraulic heads were found in both main recharge areas indicated in Fig. 1. The cross-section $A-A'$ cuts through the westerly recharge area around Ursel. In the recharge areas, the vertical downward flow through the overlying clay has relatively large Darcy velocities, in the order of some tens of mm/a. From the recharge areas on, it is converted into a subhorizontal flow in the aquifer. In cross-section $A-A'$ (Fig. 1), the horizontal flow within the aquifer has a Darcy velocity around 1.6 m/a in the recharge area. Outside the recharge areas, a slow vertical upward flow exists through the Bartonian Clay, by which groundwater is leaving the aquifer. As a result, the quantity of groundwater flowing in the aquifer is decreasing in the flow direction, leading to a gradual reduction of flow velocities as the groundwater travels further away from the recharge area. In cross-section $A-A'$ (Fig. 1), to the north of the recharge area, the horizontal Darcy flow velocity is around 0.4 m/a. In the northern part of the cross-section, it is reduced to only 0.09 m/a.

Fig. 2b shows the calculated hydraulic head distribution in the aquifer in the present situation with groundwater exploitation (Walraevens, 1988). It is observed to differ strongly from the natural condi-

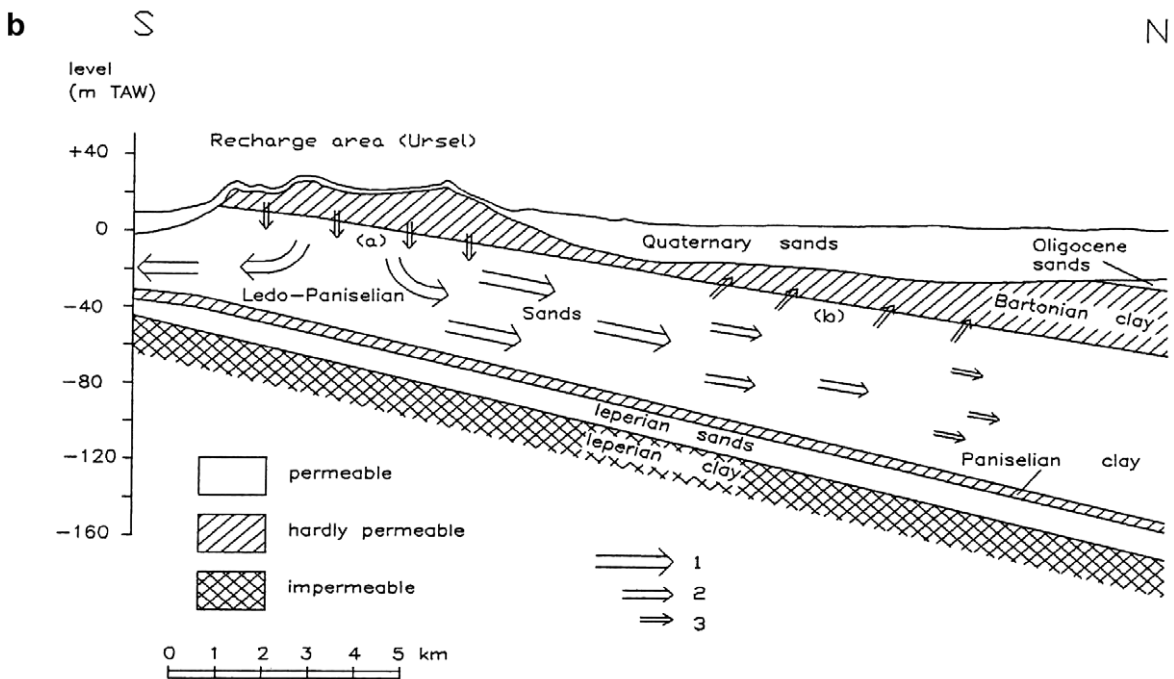
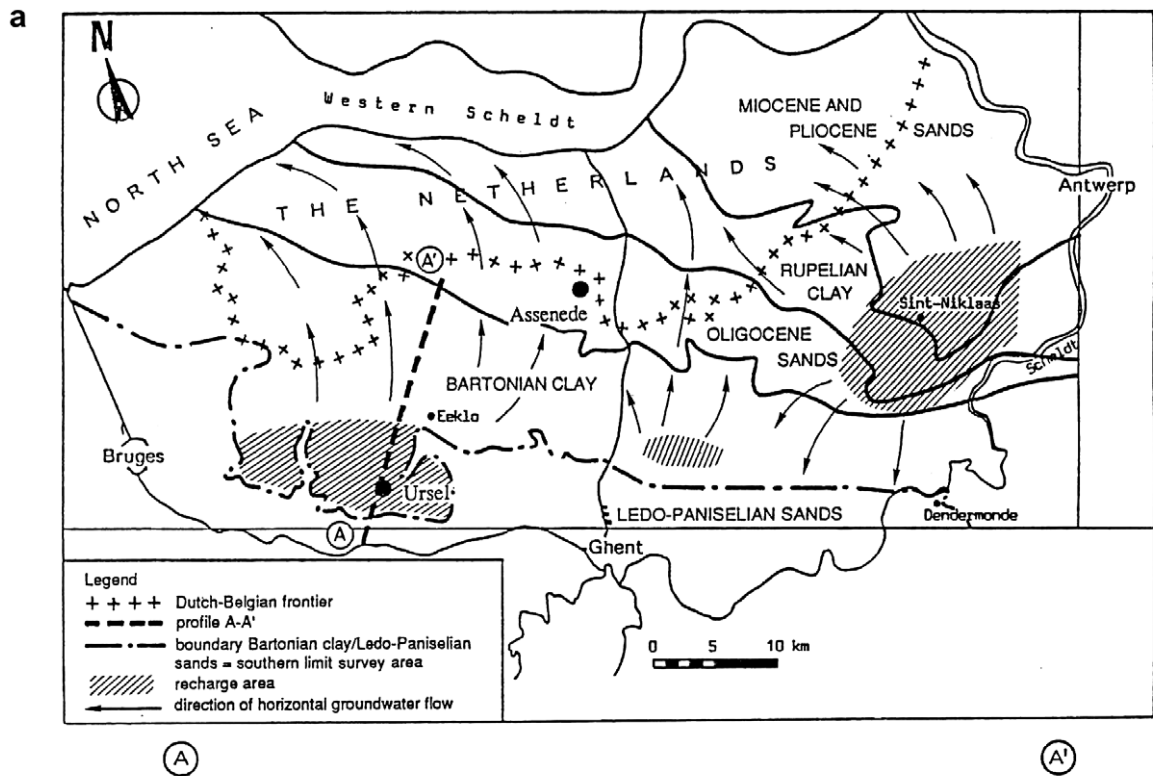


Fig. 1. Geology of the survey area and groundwater flow. Hydrogeological cross-section of Ledo-Paniselian Aquifer. Groundwater flow pathways are shown. (a) The Ledo-Paniselian Aquifer is recharged by a downward flow through the Bartonian Clay. (b) The groundwater is mostly leaving the Ledo-Paniselian Aquifer by an upward flow through the Bartonian Clay. Darcy flow velocities (indicated by arrows in figure): (1) 1.6 m/a; (2) 0.4 m/a; (3) 0.09 m/a or less (derived from the mathematical modelling of the groundwater flow in Walraevens, 1988).

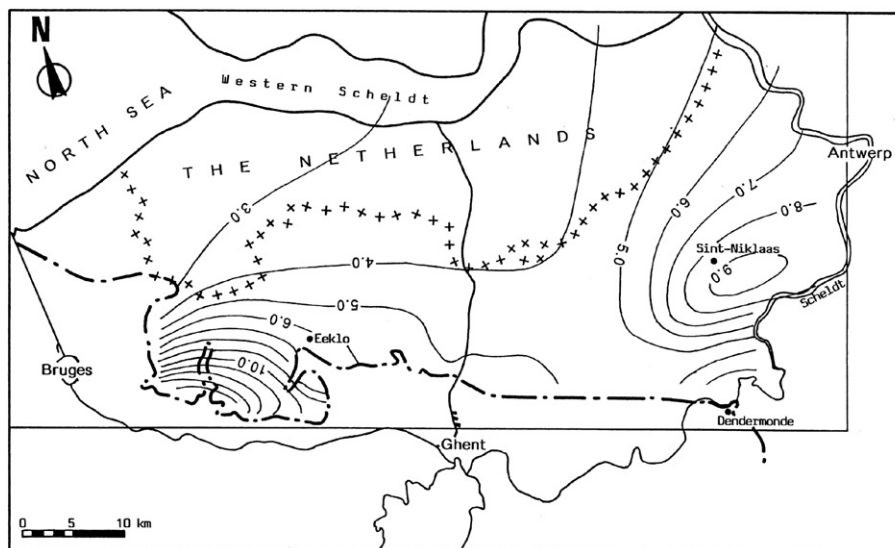


Fig. 2a. Calculated hydraulic head in the Ledo-Paniselian Aquifer in natural flow conditions. Isolines every 1.0 m (meters below sea level (b.s.l.)).

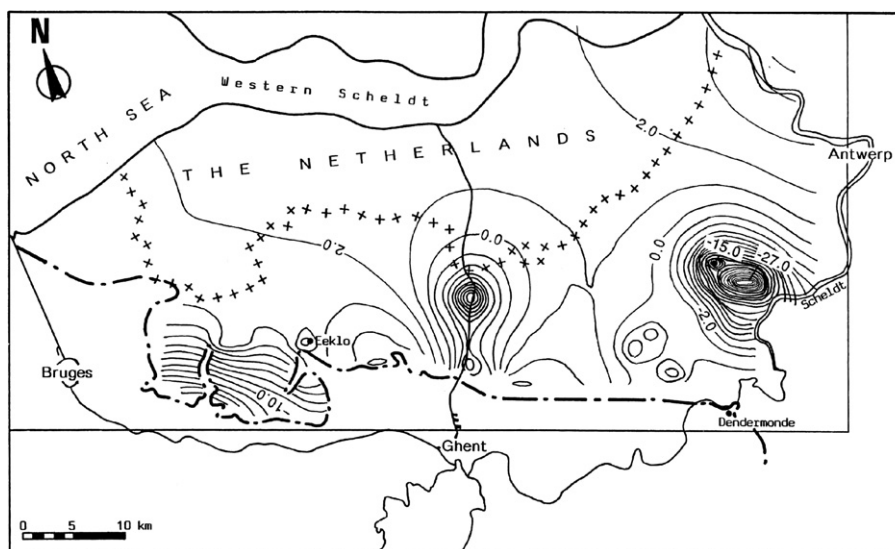


Fig. 2b. Calculated present-day hydraulic head in the Ledo-Paniselian Aquifer with pumping. Isolines every 1.0 m (meters b.s.l.).

tions, especially around the easterly recharge area, where the hydraulic head dome in natural conditions is now converted into a depression cone, with minima down to -27.0 m below sea level (b.s.l.) as a result of heavy pumping. The vertical upward flow in natural conditions has been turned into a downward flow over almost the whole survey area, thus substantially increasing aquifer recharge from above.

3. Hydrogeochemical evolution

The considered Tertiary sediments have all been deposited in a marine environment. At the end of the Tertiary, the sea regressed from the area and the present-day topography developed due to fluvial erosion. Groundwater movement was induced, by recharge of precipitation in the higher regions. Calcite dissolved in the infiltrating water, and freshen-

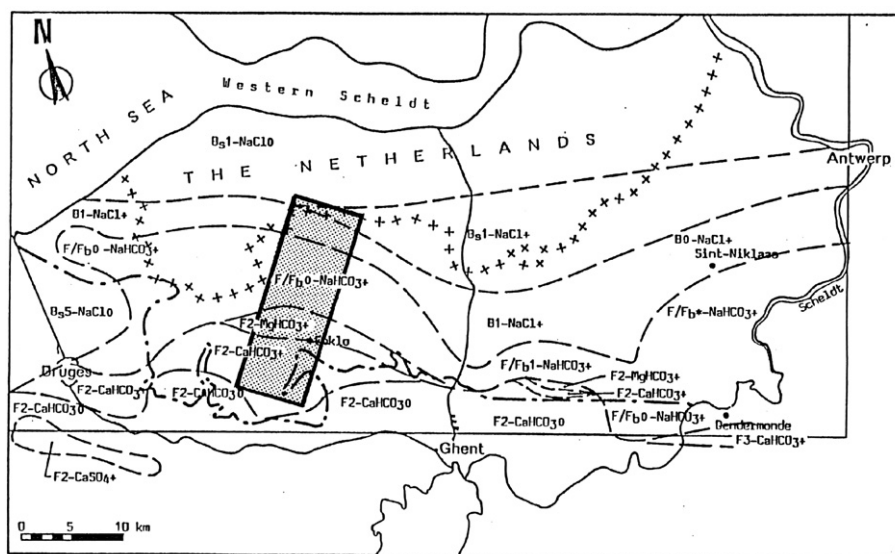


Fig. 3. Groundwater quality distribution in the Ledo-Paniselian Aquifer. Water type codes are according to the classification system of [Stuyfzand \(1991\)](#). The rectangular shaded area indicates the region of the aquifer from which observations have been taken to be compared with model results.

ing of the sediments took place, consisting of both dilution of the marine pore solution and cation exchange, the latter mainly in the Bartonian Clay in the recharge areas ([Walraevens, 1990](#)). The initially formed groundwaters were pushed to the north, in the direction of groundwater movement in the aquifer, as more precipitation was infiltrating in the recharge areas. The groundwater quality distribution in the Ledo-Paniselian Aquifer results from this evolution, whereby marine conditions are being expelled by the infiltrating fresh water ([Fig. 3](#)). In the westerly recharge area around Ussel, the groundwater type is CaHCO_3 (according to the hydrochemical classification of water types after [Stuyfzand, 1991](#)). Downward of flow (to the NNE), the MgHCO_3 type appears. More towards the north, the NaHCO_3 type is found, and still further northward the NaCl type. In the meantime, salinity increases towards the north, from fresh (F), fresh-brackish (F_b), brackish (B) to brackish-salt (B_s) (classification after [Stuyfzand, 1991](#)). Thus, in an upstream direction, progressively more freshened watertypes are found. The chromatographic sequence of cation exchange is expressed by the subsequent surplus of Na^+ , followed by K^+ and finally Mg^{2+} , resulting in the NaHCO_3 and MgHCO_3 water types. The groundwater leaking out of the clay and entering the aquifer nowadays in the recharge area around Ussel, contains only the Ca^{2+} cation in appreciable quantities.

The sequence of groundwater types observed in the Ledo-Paniselian Aquifer is in excellent agreement with the pattern of natural groundwater flow ([Fig. 2a](#)). Although recent groundwater exploitation has substantially altered the flow pattern in the aquifer ([Fig. 2b](#)), the regional distribution of groundwater chemistry is still reflecting the natural flow system.

4. Exchangeable cations in the Bartonian Clay and exchange parameters

The situation of the adsorbed cations on the Bartonian Clay minerals has been studied by [Walraevens \(1987\)](#) and [Walraevens and Lebbe \(1988\)](#). Two borehole cores, one in the recharge area at Ussel and the other at Assenede in the discharge area, were used for determining the cation exchange capacity (CEC) and exchangeable cations, especially from the clayey sediments. Some sediment samples were also taken from the Ledo-Paniselian Aquifer. The determination of CEC and the extraction of exchangeable cations were performed by means of NH_4 acetate at pH 7. As the salts soluble in water also dissolve in NH_4 acetate, they were determined separately, and the result was subtracted from the one in NH_4 acetate, delivering the exchangeable cations. Possible dissolution of calcite in NH_4 acetate at pH 7 was accounted for by attributing the surplus of the sum of obtained exchangeable Na^+ , K^+ ,

Mg^{2+} and Ca^{2+} in excess of CEC, to calcite dissolution, and subtracting this surplus from adsorbed Ca^{2+} .

CEC for the Bartonian Clay is around 27 meq/100 g; for the Ledo-Panisellian Aquifer, CEC is 5.5 meq/100 g on average. The amounts of exchangeable cations in the Bartonian Clay at Ursel and Assenede are shown in Table 1.

Table 1

Amounts of exchangeable cations (in meq/100 g) in the Bartonian Clay at the recharge area in Ursel (units a1 and Asb-a) and Assenede (units a3, a2, a1 and Asb-a)

	URSEL			ASSENEDE		
	Mean	Range	N	Mean	Range	N
CaX_2	12	5–18	15	11	7–16	18
MgX_2	13	7–19	15	10	5–17	18
NaX	0.2	0.1–0.2	15	3.9	0.5–9.0	18
KX	1.9	0.4–3.0	14	1.8	0.2–3.2	18

After Walraevens (1987). N: number of clay samples.

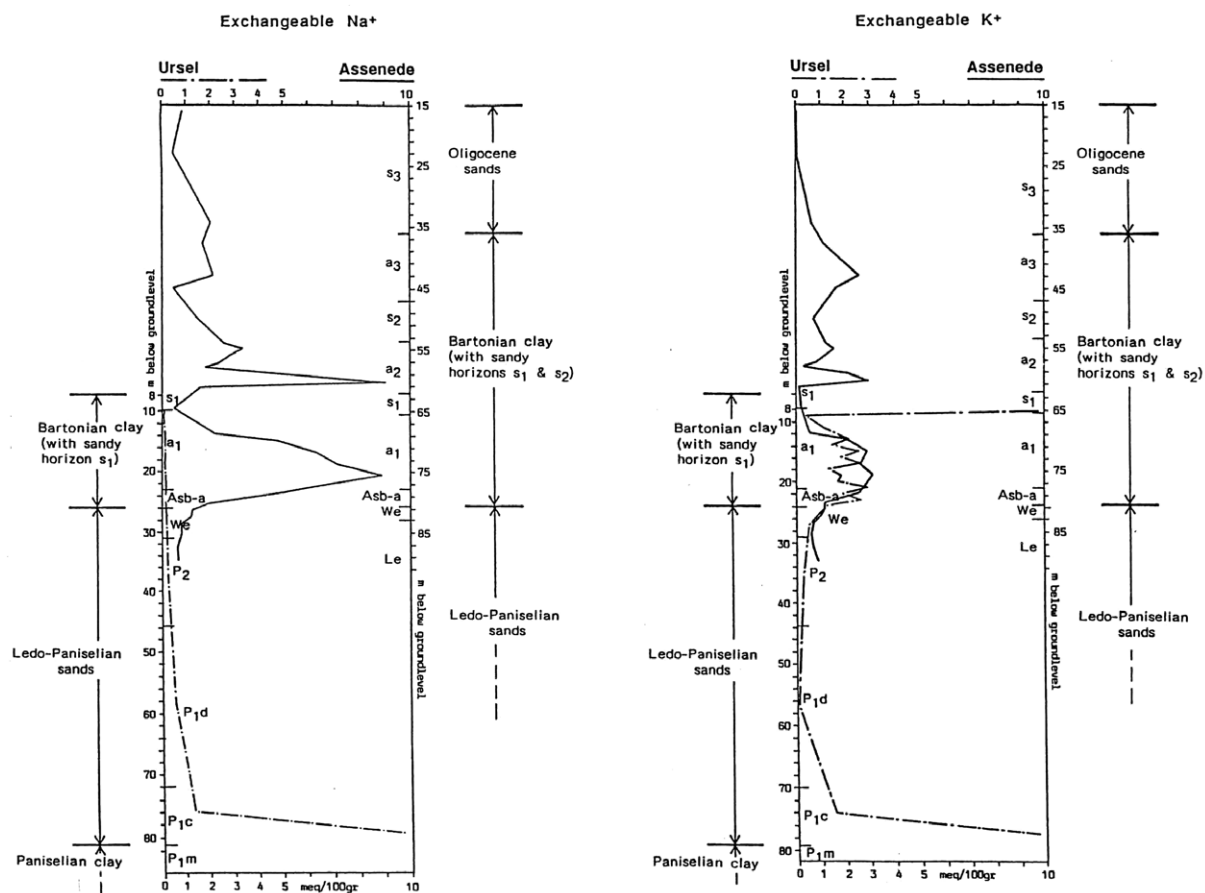


Fig. 4a. Exchangeable cations (Na^+ and K^+) in sediments of cored borings at Ursel (the recharge area) and Assenede (outside the recharge area, where marine influence still persists).

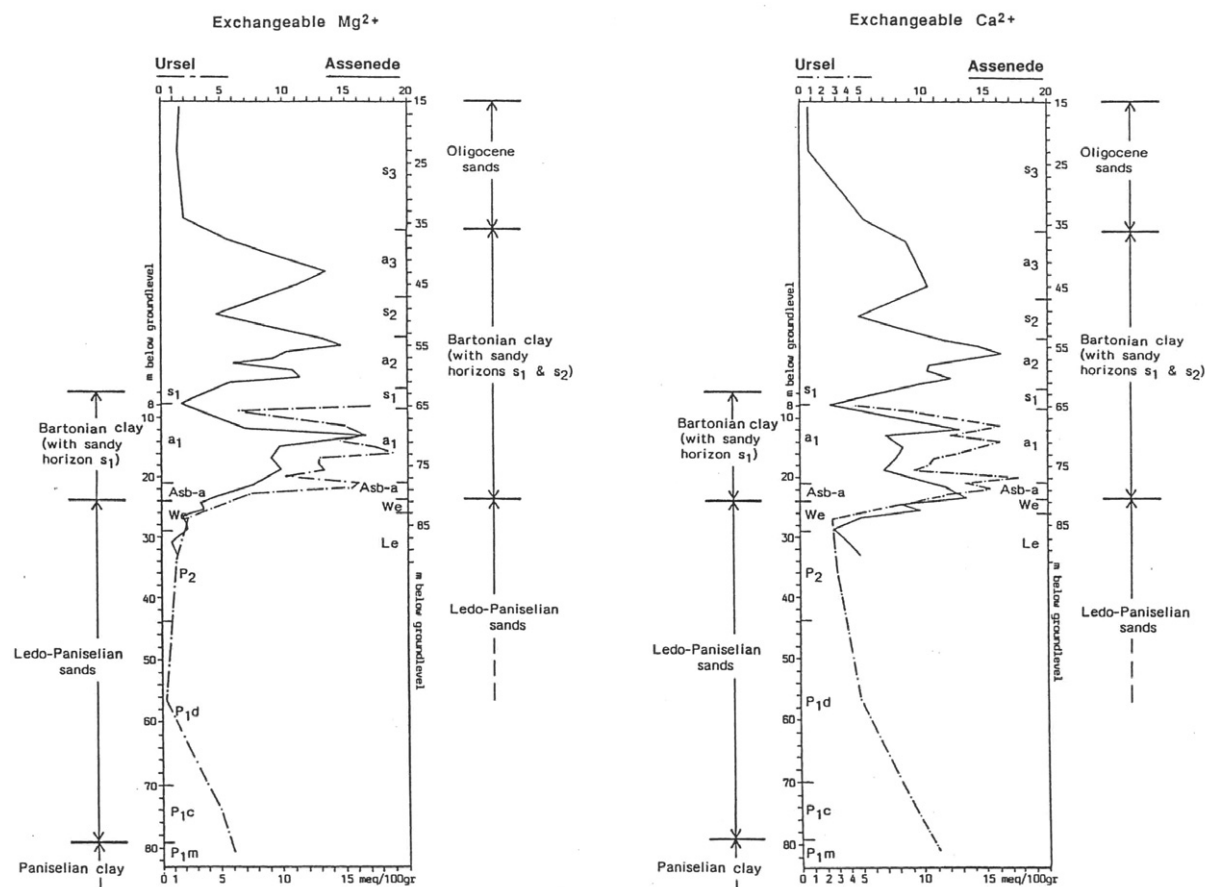


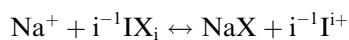
Fig. 4b. Exchangeable cations (Mg^{2+} and Ca^{2+}) in sediments of cored borings at Ursel (the recharge area) and Assenede (outside the recharge area, where marine influence still persists).

Calcium is the dominant adsorbed cation, while Na^+ is practically absent. Outside the recharge area, the marine influence still persists, expressed by a high concentration of NaX .

However, the analyzed samples of the Bartonian Clay at Ursel do not show a depletion in adsorbed Mg^{2+} (Fig. 4b). On the contrary, adsorbed Mg^{2+} shows an increase at Ursel, when compared to Assenede (Fig. 4b). This is a surprising result, as the Ledo-Paniselian Aquifer in this recharge area contains CaHCO_3 -water, indicating that the flushing of the overlying clay has practically been accomplished.

Pore water analyses are available in the bore hole drilled at Assenede. Since CEC and the different amounts of adsorbed cations in this boring are known, it is possible to estimate the exchange coefficients in the clayey sediments. The exchange coefficients have been computed with respect to Na^+ using the Gaines-Thomas convention (in Appelo

and Postma, 1993). Selecting an arbitrary high value for K_{NaX} (10^{20}), the coefficients are obtained from the general exchange reaction



with

$$K_{\text{Na/I}} = \frac{([\text{NaX}][\text{I}^{i+}]^{1/i})}{([\text{IX}_i]^{1/i}[\text{Na}^+])} \\ = \frac{(\beta_{\text{Na}}[\text{I}^{i+}]^{1/i})}{(\beta_{\text{I}}^{1/i}[\text{Na}^+])}$$

where square brackets denote activities of solutes in the pore water ($[\text{Na}^+]$ and $[\text{I}^{i+}]$) and of the exchangeable cations ($[\text{NaX}]$ and $[\text{IX}_i]$), i is the cationic charge, β_{I} is the equivalent fraction of the adsorbed cation I^{i+} with respect to CEC, and β_{Na} is the equivalent fraction of NaX with respect to CEC (where $\beta_{\text{Na}} = \text{NaX (in meq/100 g)}/\text{CEC}$).

Once $K_{\text{Na/I}}$ is solved, the association constant K_{IX_i} (which represents the reaction: $\text{I}^{i+} + i\text{X}^- \leftrightarrow \text{IX}_i$, with X^- the cation exchanger) is computed from:

Table 2

Exchange parameters for main cations. All values in $\log K_{IXz}$ ($I^{z+} + zX^- \leftrightarrow IX_z$).

	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
Bartonian clay	20.0000 ^a	20.5768 ^b	41.1728 ^b	40.8810 ^b	20.6000 ^c
Ledo-Paniselian aquifer	20.0000 ^a	20.7000 ^c 20.9317 ^d	40.8000 ^c 41.0115 ^d	40.6000 ^c 41.0510 ^d	20.6000 ^c

^a Reference value.^b Computed from data in Walraevens (1987). Mean values from 17 determinations in CEC, amounts of adsorbed Na⁺, K⁺, Ca²⁺ and Mg²⁺ and pore water analysis in samples of Bartonian clay (members a3, a2, al and Asb-a).^c Standard values in thermodynamic database (PHREEQA) of PHREEQM (Nienhuis et al., 1993).^d Computed from data in Walraevens (1987). Mean values from 4 sediment samples in Ledo-Paniselian (member Le). Not used.

$$K_{IXi} = (K_{NaX}/K_{Na/I})^i$$

The activities of individual cations ($[I^{i+}]$) have been determined from the pore water analysis using PHREEQE (Parkhurst et al., 1980). An overview with the estimated coefficients, which have been employed in modelling of the Bartonian Clay, is given in Table 2. The results are in the same order of magnitude as published data (Appelo and Postma, 1993).

For the Ledo-Paniselian Aquifer only a few sediment samples with pore water analysis were available, and all of them correspond to the top of the sandy formation. Although exchange coefficients have also been calculated and result in very similar values to those estimated for the Bartonian Clay, more accurate modelling of the aquifer was performed with the standard coefficients in the thermodynamic database (PHREEQA) of PHREEQM (Table 2). Indeed, by using these standard coefficients, the calculated chromatographic peaks of cations could better be matched with observations in the aquifer. Probably, the exchange coefficients derived from data just for the top of the aquifer are not representative for the whole thickness.

5. Geochemical modelling of freshening of the Bartonian Clay and Ledo-Paniselian Aquifer – Development of a chromatographic pattern

A geochemical mixing cell model (PHREEQM; Nienhuis et al., 1993) has been used in order to simulate the freshening of both clayey and sandy layers. A flow line was selected, starting from the top of the Bartonian Clay in the western recharge area at Ussel, and directed towards the NNE within the aquifer. Model results were compared with observations, taken from the rectangular shaded area indicated in Fig. 3.

5.1. Hydraulic schematization

The modelling was divided into two parts, because of differences between groundwater flow conditions in the Bartonian Clay compared to the Ledo-Paniselian Aquifer. Groundwater flow in the Bartonian Clay is vertical downwards; in the Ledo-Paniselian Aquifer the flow is subhorizontal. Groundwater flow velocity in the clay is of the order of some tens of meters, while the flow path in the aquifer is tens of kilometres long. Outside the recharge areas, the flow velocity within the aquifer gradually decreases in the flow direction, as part of the groundwater leaves the aquifer by vertical upward flow through the clay.

Freshening of the Bartonian Clay was simulated in a vertical column of 20 m length, divided in 4 cells of 5 m each. The successive watertypes leaking out of the Bartonian Clay were flushed through a horizontal column of the Ledo-Paniselian Aquifer, simulating the subhorizontal flow in it. In a first approach, 20 km of flow in the aquifer were modelled by dividing the flow path in 20 cells of 1 km each. Differences in flow velocity within the aquifer were accounted for in a second stage by dividing the flow path into two distinct parts. After 12 km, the succeeding watertypes flowing out of the 12th cell were injected into a new column of another 13 km length, divided in 26 cells of 0.5 km each (Fig. 5). As such 25 km of flow in the aquifer were modelled.

The vertical Darcy flow velocity through the Bartonian Clay in the recharge area was deduced by mathematical modelling of the groundwater flow (Walraevens, 1988) and found to be around 0.036 m/a (ranging between 10 mm/a and 90 mm/a). With a porosity of 0.3, the resulting pore flow velocity is 0.12 m/a.

In the Ledo-Paniselian Aquifer, the vertical water motion is converted into a subhorizontal one.

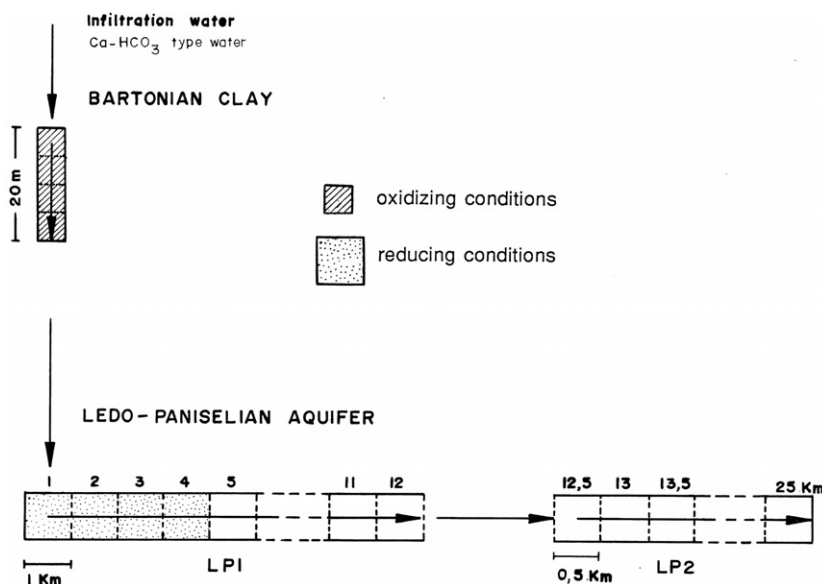


Fig. 5. Modelling approach used to flush the Bartonian Clay and the Ledo-Paniselian Aquifer. See Table 3 (model boundaries) for more information.

Within the aquifer, the flow velocity decreases from 1.6 m/a to 0.4 m/a at about 15 km downstream. An average velocity (1 m/a, equivalent to 3.3 m/a of pore flow velocity) was selected to model the evolution of groundwater composition in the aquifer in a first approach. This mean value was considered representative for the first part of the aquifer, for which an accurate modelling was performed. For the downflow part of the aquifer, it was necessary to estimate another mean value for the flow velocity

because there the flow is very limited (less than 0.1 m/a as derived from the flow model) and the former average velocity was not representative.

5.2. Chemical model

An overview of the model boundaries is given in Table 3. For both clayey and sandy layers, the initial pore water quality was sea water (analysis from Nordstrom et al., 1979) equilibrated with calcite and

Table 3
Model boundaries

	pH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NH ₄ ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	log P _{CO2}
Initial pore water	7.86	9.8	55.1	486	10.6	0.75	1.6	566	29.3	
Recharge water	7.32	2.1					4.17			-2.00

t: 11 °C (present average temperature of the groundwater in the recharge area); concentration in mmol/kg H₂O.

	Flow vel. ^a (m/year)	Dispers (m)	Diffusion (m ² /s)	Cell length (m)	Total length (m)	Time step (year)	CEC (meq/100 g)	Chemical reactions
Bartonian clay	0.12	1.5	1E-09	5	20	41.7	27	0.45 mM/cell gypsum dissolution calcite equilibrium
Ledo-P.aq. (0–20 km)	3.35	1500	–	1000	20,000	299	5.5	0.45 mM/cell SO ₄ ²⁻ reduction ^b + 0.9 mM/cell organic matter ^b
Ledo-P.aq. (12–25 km)	0.29	1500	1E-09	500	13,000	1750	5.5	calcite equilibrium calcite equilibrium

^a Pore flow velocity.

^b Only in the first 4 cells.

0.75 mM/kg H_2O of NH_4^+ production. The exchange complexes in the clay (around 27 meq/100 g) and in the sandy aquifer (around 5.5 meq/100 g) were equilibrated with this solution of constant composition. For the recharge water, pure water equilibrated with calcite and a P_{CO_2} of $10^{-2.0}$ atm, which at 11 °C means 2.1 mM $\text{Ca}(\text{HCO}_3)_2$, was used.

5.3. Freshening of the Bartonian

The Bartonian Clay column was flushed with the recharge water. A diffusion coefficient of 10^{-9} m²/s and a dispersivity value of 1.5 m were used (taken at around 10% of flow path length). During the flushing, cation exchange and calcite equilibria were maintained.

In the Bartonian Clay the presence of gypsum is observed, resulting from the oxidation of pyrite contained in the clay. This pyrite oxidation probably occurred mainly during glacial periods, when the water table was lowered (Van Camp and Walraevens, 1999) and conditions were more strongly oxidizing. Sulphate concentrations between 100 and 200 mg/L are usually found in the Ledo-Paniselian Aquifer in the southern part of the survey area, so a limited source of gypsum dissolution has been maintained during simulation (0.45 mmol/kg H_2O

per cell). This fixes the SO_4^{2-} concentration in the recharge water of the aquifer to 170 mg/L.

Fig. 6 represents the chemical composition of the different solutions which are leaving the Bartonian Clay and the distribution of the exchangeable cations in the clay during the flushing. After the clay has been flushed 75–100 times (or pore volumes), the distribution on the clay's adsorption complex is similar to the one found in the boring at Ursel. As is shown in Fig. 6, there is a loss of NaX, accompanied by an uptake of Mg^{2+} on the clay minerals, although the diluting solution in the modelling does not contain Mg^{2+} . This is due to charge effects: as the solution concentration decreases as a result of dilution, the sum of cations declines, while equilibrium with the exchanger is maintained; this induces a shift in the concentration ratio of cations with unlike charge, leading to an increase of the adsorbed divalent ion at the expense of the monovalent ion (Appelo, 1994b). So the model predicts the increase in MgX_2 , which explains the enrichment in this adsorbed cation in Ursel with respect to the Assenede boring. At this stage almost all NaX is exhausted, while a substantial amount of KX still remains, again consistent with the situation observed at the Ursel boring.

At that moment (after 75–100 pore volumes have been flushed) the pore water solution which is leav-

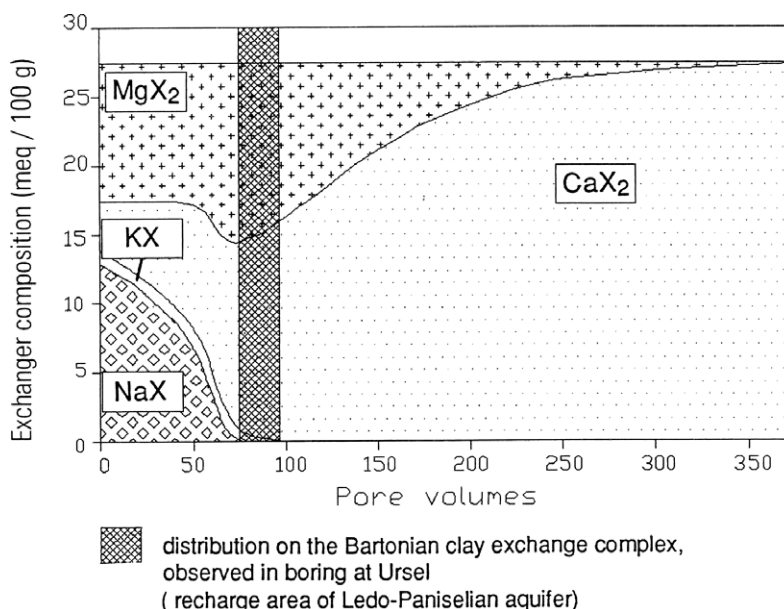


Fig. 6a. Calculated amounts of exchangeable cations (in meq/100 g). The shaded area indicates the approximate present situation of the exchange complex in the Bartonian Clay at Ursel.

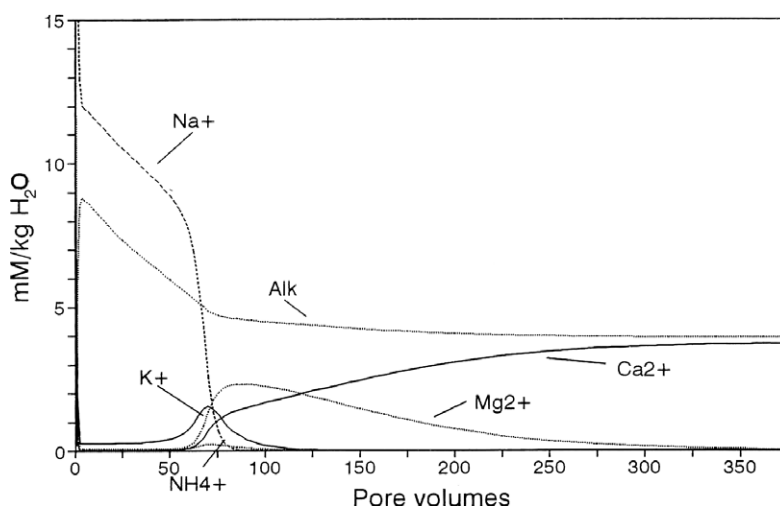


Fig. 6b. Calculated chemical composition of the pore water (in mmol/kg H₂O, alkalinity in meq/L) in the Bartonian Clay during the flushing (concentrations above 15 mmol/kg in the first flushes are not shown).

ing the Bartonian Clay contains Ca²⁺ and Mg²⁺ as main cations, with an appreciable K⁺ concentration and no significant Na⁺ content. This water is very different from the one found at present in the Ursel recharge area of the Ledo-Paniselian Aquifer, in which Mg²⁺ and K⁺ are almost absent. The clay must be flushed 300–350 times (or pore volumes) to obtain a water quality similar to the one found in the recharge area of the aquifer (fresh and CaHCO₃-type). This may be the result of preferential flowpaths in the Bartonian Clay where the flow is faster. The presence of preferential pathways has already been suggested to account for the relatively high hydraulic conductivities of the Bartonian Clay (on the order of 10⁻⁹ m/s), which were deduced from the groundwater flow model calibration, and which did not agree with laboratory values (Walraevens, 1990). The flow line in the analyzed boring must be part of a slower pathway and the freshening here is still in progress (Walraevens and Cardenal, 1994).

From Fig. 6 it is clear how succeeding watertypes show a chromatographic pattern during the freshening of the clay: in the first flushes, the NaCl-water-type appears, then sequentially, NaHCO₃, NaKHCO₃, MgHCO₃, CaMgHCO₃ and finally, CaHCO₃-type. The different watertypes obtained in this way are those observed at present in the Ledo-Paniselian Aquifer and other detritic aquifers (Aquia Aquifer in Maryland, USA – Appelo, 1994a – and Dutch polders – Beekman, 1991), where cation exchange processes are the main con-

trol in the groundwater quality during the flushing of brackish or salt water aquifers by fresh water intrusion.

5.4. Freshening of the Ledo-Paniselian Aquifer

The succeeding watertypes leaking out of the Bartonian Clay have been used to model the horizontal column of the Ledo-Paniselian Aquifer. In order to account for the different flow velocities in both columns, several water compositions were selected and proportionally flushed. The total time modelled in the aquifer was the same as for the Bartonian Clay. Fig. 7 illustrates this procedure. This figure represents the Mg²⁺ and K⁺ concentrations of the water leaving the clay column. The rectangles indicate the average Mg²⁺ and K⁺ concentrations leached out of the clay during succeeding periods of time steps (a time step or shift in a mixing cell model means that the solutions reside a time Δt in the cell, equilibrating with the cell matrix, and then, the water volume is poured into the next cell mixing with it; Appelo and Willemssen, 1987; Appelo and Postma, 1993). In the example shown in Fig. 7, between shifts 700–900 the water leaving the clay has a Mg²⁺ content near 0.7 mM/kg H₂O. These 200 shifts take 8.34 ka because each shift in the modelling of the clay column is 41.7 a. In the Ledo-Paniselian Aquifer each shift takes 298.5 a, so 8.34 ka are equivalent to 28 shifts. This means that a water composition leaving the clay during 200 time steps will be introduced in the aquifer during 28

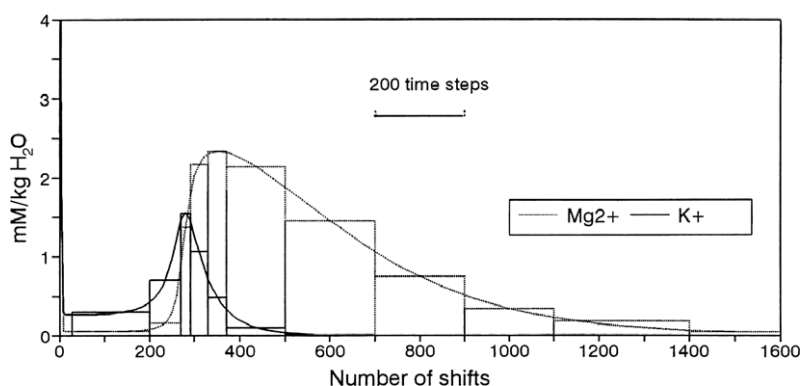


Fig. 7. Calculated K^+ (solid line) and Mg^{2+} (dashed line) contents of the pore water leaking out of the Bartonian Clay during the flushing. Rectangles represent the selected K^+ and Mg^{2+} contents used to flush the Ledo-Paniselian Aquifer during specified time steps. The same is done for the other elements. This allows the use of only 13 water compositions (Table 4) instead of the 1500 water compositions that are leaking out of the clay.

shifts. The total time used to model the clay will be the same as for the aquifer. So the 1500 shifts employed to freshen the Bartonian Clay are equivalent to 210 shifts in the aquifer and instead of using 1500 water compositions to flush the aquifer, only 13 representative samples are employed (Table 4).

With these succeeding water compositions, it has been necessary to flush the aquifer 11 times to obtain the peaks of the main cations at the right positions along the flow path in the aquifer (Fig. 8). The model dispersivity was adapted to fit the observed shape of the peaks, to a value of 1500 m; this value is consistent with the fraction of the flow path length used for modelling the Bartonian Clay. Because the average pore water flow velocity in the aquifer is more than 3 m/a, diffusion was neglected. During the flushing, cation exchange

and calcite equilibria were maintained. The modelled distribution of the main cations Na^+ , K^+ , Mg^{2+} and Ca^{2+} is independent on most other processes that also influence the water chemistry in this aquifer (initial P_{CO_2} , gypsum dissolution in the clay, sulphate reduction in the aquifer) and predominantly related to the chromatographic separation. In fact, Cardenal and Walraevens (1994) obtained similar results (with respect to the main cations) using an initial P_{CO_2} of $10^{-2.5}$ and the standard exchange coefficients (in PHREEQM) during freshening of the Bartonian Clay. Yet, calcite dissolution is important: cation exchange causes a second stage of calcite dissolution, as Ca^{2+} is removed from the solution to become adsorbed, and the groundwater becomes undersaturated with respect to calcite (Walraevens, 1987). This is especially important in

Table 4

Selected water compositions of the pore water leaving the Bartonian Clay used to freshen the Ledo-Paniselian Aquifer

T.S. Bart.	T.S. Led.	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	TIC	SO_4^{2-}	Cl^-	pH
1	1	9.90	55.26	485.80	10.59	0.750	1.52	29.71	565.80	7.809
29	4	0.01	0.05	12.02	0.26	0.072	7.03	1.80	0.02	9.821
170	24	0.02	0.05	9.73	0.30	0.054	5.91	1.80	0.00	9.433
70	10	0.07	0.15	7.87	0.70	0.088	5.35	1.80	0.00	8.804
20	3	0.70	1.37	2.59	1.55	0.213	5.04	1.80	0.00	7.830
40	6	1.18	2.17	0.34	1.06	0.181	4.93	1.80	0.00	7.619
40	6	1.45	2.34	0.03	0.48	0.109	4.88	1.80	0.00	7.542
130	18	1.82	2.14	0.00	0.01	0.004	4.72	1.80	0.00	7.338
200	28	2.46	1.46	0.00	0.10	0.036	4.82	1.80	0.00	7.454
200	28	3.10	0.74	0.00	0.00	0.000	4.63	1.80	0.00	7.254
200	28	3.46	0.33	0.00	0.00	0.000	4.59	1.80	0.00	7.213
300	42	3.60	0.18	0.00	0.00	0.000	4.57	1.80	0.00	7.199
100	14	3.73	0.04	0.00	0.00	0.000	4.56	1.80	0.00	7.187

T.S. Bart.: number of time steps (41.7 a/step) for the Bartonian Clay during which the mentioned average water composition is considered to have been leaking from the clay. T.S. Led.: corresponding time steps (299 a/step) for the Ledo-Paniselian Aquifer.

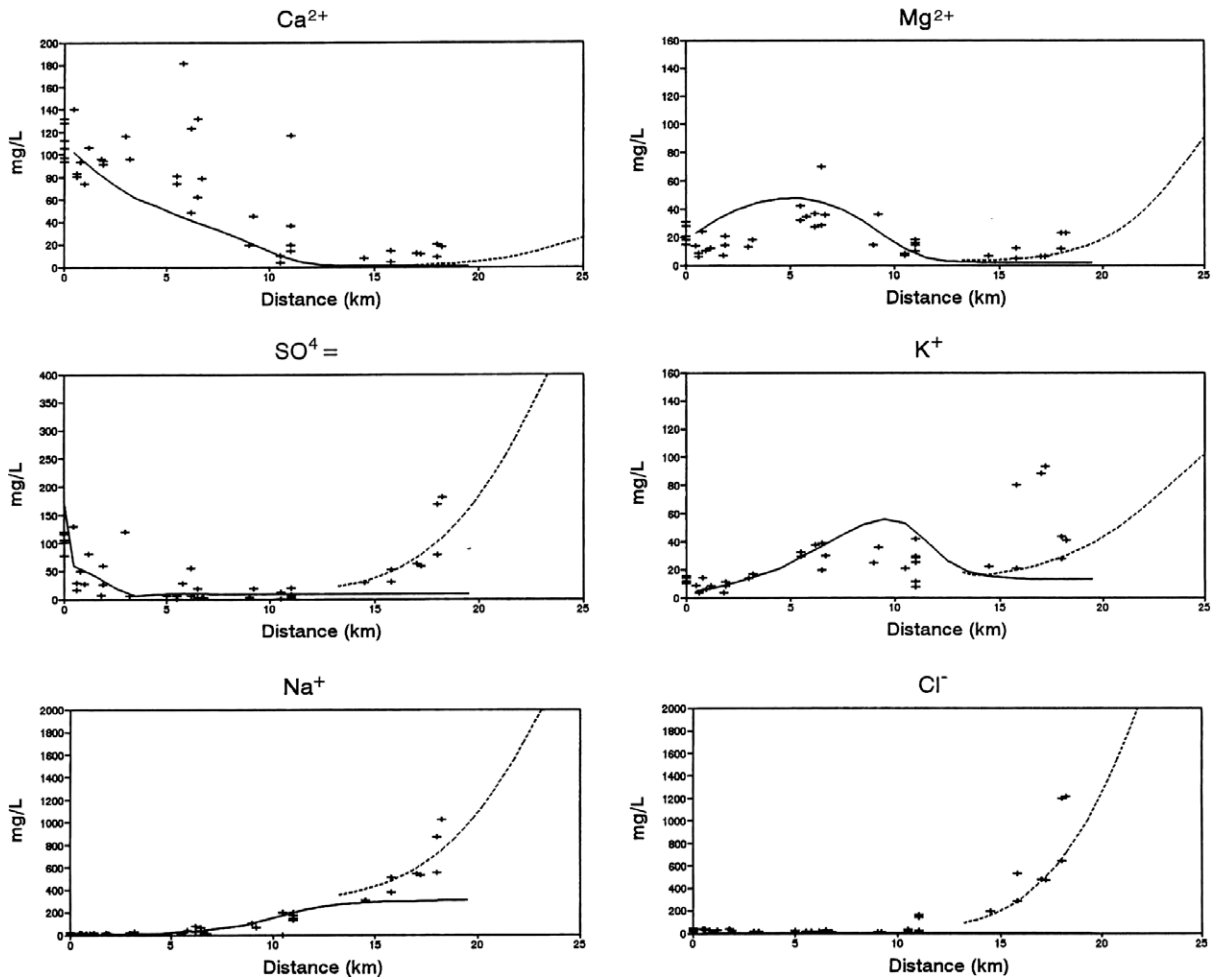


Fig. 8. Ca^{2+} , Mg^{2+} , SO_4^{2-} , K^+ , Na^+ and Cl^- contents in the groundwater of the Ledo-Paniselian Aquifer along the flow path. Crosses are field data; solid lines represent calculated concentrations for the first part of the aquifer (LP1; pore flow velocity 3.3 m/a); dashed lines are calculations for the last 12–25 km of the aquifer (LP2; pore flow velocity used of 0.3 m/a).

the NaHCO_3 watertype, which is the main watertype giving evidence of cation exchange. As the produced Ca^{2+} is subsequently adsorbed, while Na^+ is desorbed, high Na^+ concentrations result in this way. Despite this second stage of calcite dissolution, Ca^{2+} concentrations in groundwater remain low because of cation exchange.

The distribution of alkalinity, expressed as mg/L of HCO_3^- , has also been calculated (Fig. 9). Walraevens (1987) has shown the relation between alkalinity and the extent of cation exchange in the Ledo-Paniselian Aquifer. In order to maintain equilibrium with calcite, which is present in the sediment, this mineral dissolves when Ca^{2+} is adsorbed on the clays. But the alkalinity values modelled with only calcite equilibrium (200–400 mg/L) are clearly lower than those

observed. The modelling of alkalinity is improved by considering SO_4 reduction in the first 4 cells of the aquifer column. The occurrence of SO_4 reduction is supported by the detection of H_2S in the recharge area of the aquifer (Walraevens, 1987). The SO_4 reduction causes most of the SO_4^{2-} to disappear a few km downstream (Fig. 8). It has been modelled by adding 3.6 mM/kg H_2O of organic matter, with redox state equal to zero, in the first 4 km of the aquifer. This allows improving the modelling of the alkalinity distribution in the aquifer: in the first 4 km there is an increase from 300 to 400 mg/L of HCO_3^- ; then the alkalinity becomes more stable (the slope decreases) and starting from 9 km, in the NaHCO_3 -type dominated water, the alkalinity rises again.

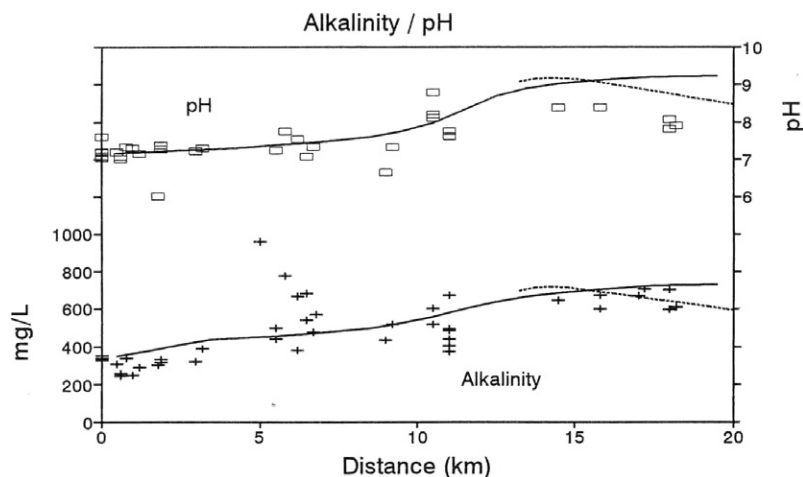


Fig. 9. Alkalinity (expressed as mg/L of HCO_3^-) and pH distributions in the groundwater of the Ledo-Paniselian Aquifer along the flow path. Crosses (HCO_3^-) and squares (pH) are field data; solid lines represent calculations for the first part of the aquifer (LP1; pore flow velocity of 3.3 m/a); dashed lines are calculations for the last 12–25 km of the aquifer (LP2; pore flow velocity of 0.3 m/a).

The pH follows a similar trend in the Ledo-Paniselian Aquifer (Fig. 9). Typical NaHCO_3 -type waters have pH values around 8.5 (Foster, 1950). The pH has been adequately modelled although slightly higher values, near 9.0, have also been computed in the last 5 km.

The NH_4^+ content also rises between 6 and 12 km (Fig. 10), clearly associated with the increased Mg and K concentrations. Also this raised NH_4^+ content is attributed by Walraevens (1987, 1990) to cation exchange. However, sea water, which is the source

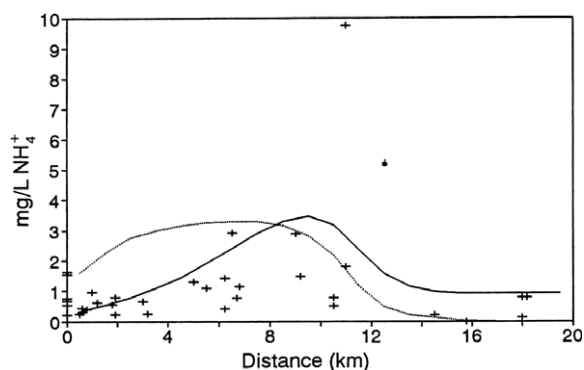
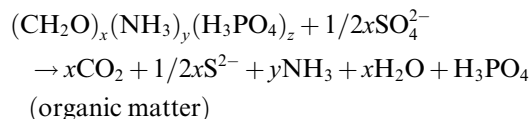


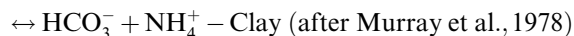
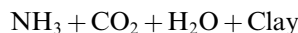
Fig. 10. NH_4^+ content in the groundwater of the Ledo-Paniselian Aquifer along the flow path. Crosses are field data; the solid line represents the modelling results for $\text{NH}_4^+/\text{Ca}^{2+}$ exchange, considering an initial production of NH_4^+ under marine syndimentary conditions and subsequent adsorption in the sediment at the sea bottom, according to Murray et al. (1978). The dashed line represents modelled NH_4^+ contents when considering NH_4^+ production in the present fresh and reducing conditions in the recharge area of the Ledo-Paniselian Aquifer.

for the exchanged Na^+ , K^+ and Mg^{2+} , does not contain a lot of NH_4^+ .

Sayles and Manheim (1975) state that diagenetic changes of pore waters in terrigenous sediments on the seafloor are dominated by reactions with organic matter, such as the formation of NH_4^+ . Murray et al. (1978), describe the subsequent adsorption of NH_4^+ onto the clay surfaces



and



The adsorbed NH_4^+ can then later be delivered to the percolating fresh water, in exchange for Ca^{2+} . With an initial NH_4^+ production of 0.75 mM/kg H_2O , it is possible to explain the concentrations above 2 mg/L found in some parts of the aquifer. The modelled peak appears associated to the K^+ peak, just between the MgHCO_3 and NaHCO_3 -types.

It is also possible to explain the NH_4^+ production by the reducing conditions existing in the first few kilometres of flow path in the aquifer. Ammonium can be produced when organic matter is being oxidized incompletely. The conditions should be sufficiently reducing to cause the appearance of NH_4^+ and not NO_2^- nor NO_3^- , that originate in more oxi-

dizing conditions. In fact, to the south of the study area, where the Ledo-Paniselian Aquifer is unconfined, appropriate conditions explain the occurrence of high NH_4^+ contents ($>1 \text{ mg/L}$) in some parts of it. Similarly it is possible to model NH_4^+ production associated with the reducing conditions causing SO_4 reduction in the first 4 km of the aquifer. If at the same time NH_4^+ is produced, advective transport and also adsorption onto the clay minerals could perhaps reproduce the observed peak. However, modelling this way, the NH_4^+ content rises immediately in the first 4 km; as a result of advective transport, the concentration is stable until the 10th km; then it decreases by adsorption onto the exchange complex. The observed peak is not accurately modelled this way and it is not possible to fit the field data (Fig. 10).

Both processes can contribute to the NH_4^+ distribution in the aquifer, but the observed rise of its concentration, associated to the K^+ peak, is better explained and more accurately modelled by initial NH_4^+ production in the sea bottom sediment in contact with pore sea water, subsequent adsorption onto the clay minerals and later exchange for Ca^{2+} from the infiltrating fresh water.

5.5. Freshening of the aquifer in the northern part

Although the model seems valid for the first 12 km, the field data cannot be matched for the last part of the aquifer, where all parameters increase in concentration. This disagreement is related to the decreasing flow velocity in the downstream section. In the northern part, water seeps upward through the Bartonian Clay, and flushing of the aquifer is less extensive than calculated by the model which considers a uniform flow velocity.

A smaller flow velocity is needed to fit the field data in the northern part of the aquifer. A methodology similar to the one employed in the transition from Bartonian Clay to Ledo-Paniselian Aquifer,

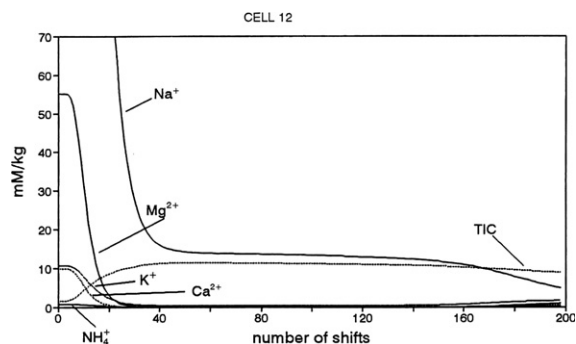


Fig. 11. Chemical composition (mmol/kg H_2O) of the pore water leaving the 12th cell (12 km downward the flow) of the Ledo-Paniselian Aquifer column. Six representative analyses of these water compositions were selected in order to flush another column of the aquifer and model the northern part of the survey area.

was utilized to adapt both parts of the aquifer with significantly different velocities. The 12th cell was selected as the boundary between both parts. The evolution of the water quality in this cell during freshening of the aquifer has been represented in Fig. 11. Six water compositions were considered as representative (Table 5) and were proportionally flushed through another column of 13 km with a cell length of 500 m. Cell 12 is thus cell 0 of the new column. With a flow velocity of 0.09 m/a (data from Walraevens, 1987), equivalent to 0.29 m/a of pore flow velocity, each time step in the new column is 1.75 ka.

Summarizing, the complete modelling follows the steps (cfr. Fig. 5):

First, transition from Bartonian Clay to Ledo-Paniselian Aquifer:

$$(41.7\text{a}/\text{shift}_B)/(298.5\text{a}/\text{shift}_{LP1}) = 0.14$$

$$\text{So, } 1500 \text{ shifts}_B * 0.14 \Rightarrow 210 \text{ shifts}_{LP1}$$

Then transition from the first 12 km in the aquifer to the downstream part of it:

$$(298.5\text{a}/\text{shift}_{LP1})/(1750\text{a}/\text{shift}_{LP2}) = 0.17$$

Table 5

Selected water compositions of the pore water leaving the 12th cell in the Ledo-Paniselian Aquifer

T.S. LP1.	T.S. LP2	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	TIC	SO_4^{2-}	Cl^-	pH
6	1	9.78	55.09	485.40	10.58	0.750	1.52	29.27	565.80	7.811
19	3	1.13	8.44	170.80	3.87	0.323	5.90	10.17	170.60	8.024
25	4	0.02	0.11	16.90	0.39	0.061	11.20	1.97	3.37	9.190
100	17	0.02	0.06	11.48	0.28	0.052	9.02	1.80	0.00	9.422
50	9	0.02	0.06	10.19	0.38	0.057	8.42	1.80	0.00	9.155
12	2	0.13	0.30	6.98	1.26	0.163	7.80	1.80	0.00	8.322

These water compositions have been used to freshen the northern part of the aquifer (between 12 and 25 km). T.S. LP1: time steps for the first part of the aquifer (299 a/step). T.S. LP2: time steps (1.75 ka/step) for the northern part of the aquifer.

So, $210 \text{ shifts}_{\text{LP1}} * 0.17 \Rightarrow 36 \text{ shifts}_{\text{LP2}}$

Here shifts_{B} refers to shifts in the Bartonian Clay, LP1 to the previous modelling of the aquifer and LP2 to the modelling of the last part of the aquifer. The total time modelled is 6.3 ka in the three simulations. After 36 time steps (LP2), the modelling can reproduce accurately the observations in the northern part of the survey area (Figs. 8 and 9).

In this part of the aquifer, cation exchange is less important and mixed water types are found. In these conditions, very limited flow combined to mixing with fossil sea water that remains stationary to the north of the survey area, takes place and diffusion cannot be neglected. A gradual dilution of the initial pore sea water occurs. So mixed hydrochemical facies are developed and all elements, especially Na^+ , Cl^- and SO_4^{2-} increase.

6. Conclusions

By means of a reaction transport model the freshening of marine sediments has been studied. This has confirmed the presence of preferential pathways in the Tertiary Bartonian Clay, suggested by groundwater flow modelling. The Tertiary sandy Ledo-Paniselian Aquifer is recharged through percolation of this clay. The modelling was adapted to the particular flow conditions in the sediments: a slow and vertical downward flow through a thin clay layer (20 m thick) is converted into a faster and subhorizontal flow through the aquifer.

The modelling technique employed has confirmed the control of cation exchange on water quality in the Ledo-Paniselian Aquifer and the importance not only of $\text{Ca}^{2+}/\text{Na}^+$ exchange, but also of $\text{Ca}^{2+}/\text{K}^+$, $\text{Ca}^{2+}/\text{Mg}^{2+}$ and even $\text{Ca}^{2+}/\text{NH}_4^+$ exchange. The groundwater quality distribution in the aquifer is the result of a spatial separation of the marine cations being sequentially desorbed by the recharging fresh water (CaHCO_3 -type water), revealing a complete chromatographic pattern. This chromatographic pattern has developed mainly in the overlying Bartonian Clay during the vertical downward flow that takes place in the recharge area. In the Ledo-Paniselian Aquifer, exchange reactions (although less important than in the clay) and SO_4 reduction occur, and the cation peaks are broadened by dispersion. However, in the downstream northern parts of the aquifer where flow is limited, cation exchange processes are less effective and gradual dilution of stationary fossil seawater occurs.

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